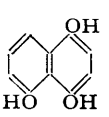
352. *The Structure of β-Hydrojuglone and Related Compounds. Keto–Enols of the Naphthalene Series.*

By R. H. Thomson.

β-Hydrojuglone is shown to be 5-hydroxy-1 : 4-diketo-1 : 2 : 3 : 4-tetrahydronaphthalene (IV). The simplest members of this series (VI; R = H or Me) are stable compounds, but in general these diketones exhibit few ketonic properties; under most reaction conditions they enolise rapidly and only derivatives of the corresponding polyhydroxynaphthalenes are obtained.

Juglone (5-hydroxy-1 : 4-naphthaquinone) occurs in walnut tissues in a reduced form and may be isolated by solvent-extraction and oxidation. Two isomeric reduction products, α- and β-hydrojuglone, were isolated by Mylius (*Ber.*, 1884, **17**, 2441; 1885, **18**, 2567) and their existence as glycosides was postulated by early workers. Daglish (*Biochem. J.*, in the press) has now identified the 5-glucoside of α-hydrojuglone as a natural product, but careful examination of a large number of walnut extracts by chromatographic and spectrographic analysis failed to detect the β-isomer or a derivative. Mylius, in fact, is the only worker who has obtained β-hydrojuglone from natural sources, and the present work shows that his method of extraction would convert part of the α-hydrojuglone into the β-form.

Mylius showed that α-hydrojuglone was readily transformed into the β-isomer by heating it above its melting point; both isomers formed the same triacetate and the same tribenzoate, but, whereas the α-compound was readily oxidised to juglone and was therefore (I), β-hydrojuglone was not a quinol. Later, Willstätter and Wheeler (*Ber.*, 1914, **47**, 2796) observed that β-hydrojuglone formed monocarbonyl derivatives, indicating that the hydrojuglones were keto–enol tautomers, and they proposed structure (II) or (III) for β-hydrojuglone. Similar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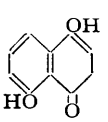
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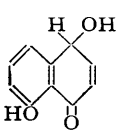
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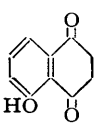
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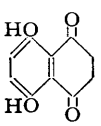
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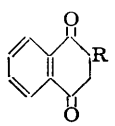

(VI.)

substances have been obtained from naphthazarin (5 : 8-dihydroxy-1 : 4-naphthaquinone). Thus Zincke and Schmidt (*Annalen*, 1895, **286**, 27) reduced naphthazarin with acid stannous chloride and obtained a product which they believed to be a tetrahydroxynaphthalene. Wheeler and Edwards (*J. Amer. Chem. Soc.*, 1916, **38**, 387) demonstrated the ketonic character

of this substance by the preparation of a series of monocarbonyl derivatives and an impure bisphenylsemicarbazone, and the structure 5 : 8-dihydroxy-1 : 4-diketo-1 : 2 : 3 : 4-tetrahydronaphthalene (V) was confirmed when Zahn and Ochwat (*Annalen*, 1928, **462**, 72) synthesised the material by condensing quinol with succinic anhydride. On these grounds Zahn and Ochwat (in a footnote to the same paper) proposed the diketo-structure (IV) for β-hydrojuglone. This is now confirmed.

Analogous "β-hydronaphthaquinones" have been prepared by Madinaveitia and Olay (*Anal. Fis. Quím.*, 1933, **31**, 134) and Olay (*Rev. Acad. Cienc. Madrid*, 1935, **32**, 384) from 1 : 4-naphthaquinone, 2-methyl-1 : 4-naphthaquinone, and 5-hydroxy-2-methyl-1 : 4-naphthaquinone (plumbagin), by fusion of their normal quinols. As these compounds formed monocarbonyl derivatives, and attempts to prepare diketo-derivatives were unsuccessful, they were considered to be half-enolised quinones of the same type as (II), or, less likely, (III). The products from 1 : 4-naphthaquinone and 2-methyl-1 : 4-naphthaquinone have now been re-examined, along with β-hydrojuglone (plumbagin was not available). By analogy with Zahn and Ochwat's suggestion these compounds should have the diketone structure (VI; R = H or Me).

The structures put forward by Willstätter and Wheeler, and by Olay, contain enolic hydroxyl groups but very little evidence has been obtained in favour of this. With two exceptions, all the tests applied (see Experimental section) were negative. Attempts to prepare hydroxyl derivatives failed unless catalysts were used which brought about complete enolisation. The compounds dissolve slowly in dilute sodium hydroxide solution (much faster than anthrone however), but this is obviously preceded by enolisation since the ketones may be quantitatively converted into the enols by dissolution in cold dilute alkali followed by acidification. Determination of active hydrogen gave some indication of the presence of a hydroxy-group but the results were anomalous and will be discussed later. Although β-hydrojuglone contains a phenolic group it fails to react with diazomethane or with phenyl *iso*cyanate in absence of a catalyst. This is parallel to the behaviour of juglone and may be ascribed to intramolecular hydrogen bonding.

The failure of the earlier workers to prepare dicarbonyl derivatives from these keto-compounds has been encountered again, but di-*p*-nitrophenylhydrazones have been obtained from Olay's ketones (VI; R = H or Me). Positive chemical proof of the diketo-structure of β-hydrojuglone has not been obtained, but substantial evidence is provided by the absorption spectra.

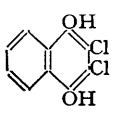
The infra-red absorption of the three ketones and the corresponding 1 : 4-naphthaquinones have been determined for a mull with liquid paraffin. The results are presented in the Table (for the spectra of 1 : 4-naphthaquinone and 2-methyl-1 : 4-naphthaquinone, cf. Rosenkrantz, *J. Biol. Chem.*, 1948, **173**, 441) :

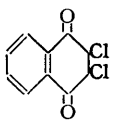
Compound.	Frequency ($cm.^{-1}$). C=O.		OH.	Compound.	Frequency ($cm.^{-1}$). C=O.		OH.
(IV)	1677	1628	Absent	Juglone	1667	1643	Absent
(VI; R = H)	1673		,,	1 : 4-Naphthaquinone	1660		,,
(VI; R = Me) ...	1688		,,	2-Methyl-1 : 4-naphthaquinone	1661		,,

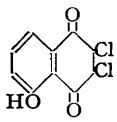
The important features of the spectra from which conclusions may be drawn are the positions of the characteristic carbonyl and hydroxyl bands in the 6-μ. and 3-μ. regions respectively. The spectra of the ketones and the corresponding quinones show only minor differences in these regions, and in all cases, including β-hydrojuglone, there is no hydroxyl band in the spectrum near 3400 $cm.^{-1}$. This eliminates the enolic structures suggested by Olay, and Willstätter and Wheeler, and the compounds must therefore have the 1 : 4-diketo-1 : 2 : 3 : 4-tetrahydronaphthalene structures (IV and VI; R = H or Me). It was considered that the monoketo-form might possibly exist to some extent when the compounds were in solution and not in the crystalline state. However examination of Olay's compounds in dilute carbon tetrachloride solution (2%) showed again the absence of a hydroxyl band. The suppression of the hydroxyl band in juglone and β-hydrojuglone is caused by intramolecular hydrogen bonding and has been observed previously in *peri*-hydroxy-1 : 4-naphthaquinones (Weiss and Ford, *Arch. Biochem.*, 1949, **22**, 288) and *peri*-hydroxyanthraquinones (Flett, *J.*, 1948, 1441). The carbonyl stretching vibration frequency is also affected in such compounds, and juglone and β-hydrojuglone, like 1-hydroxyanthraquinone, show two carbonyl frequencies.

Further evidence in support of the structure of these diketones is obtained from their ultra-violet absorption spectra. The spectra of naphthaquinone dichloride (VIII) and juglone

dichloride (IX) were determined for comparison. Figs. 1—3 show that the curves of Olay's ketones (VI; R = H or Me) are similar to that of (VIII), and the absorption characteristics


VII.)


(VIII.)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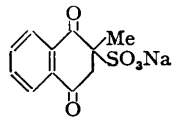
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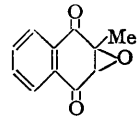

(XI.)

of β-hydrojuglone are of the same type as those of (IX), indicating their structural similarity. Furthermore, Carmack, Moore, and Balis (*J. Amer. Chem. Soc.*, 1950, **72**, 844) have shown

FIG. 1. FIG. 2.

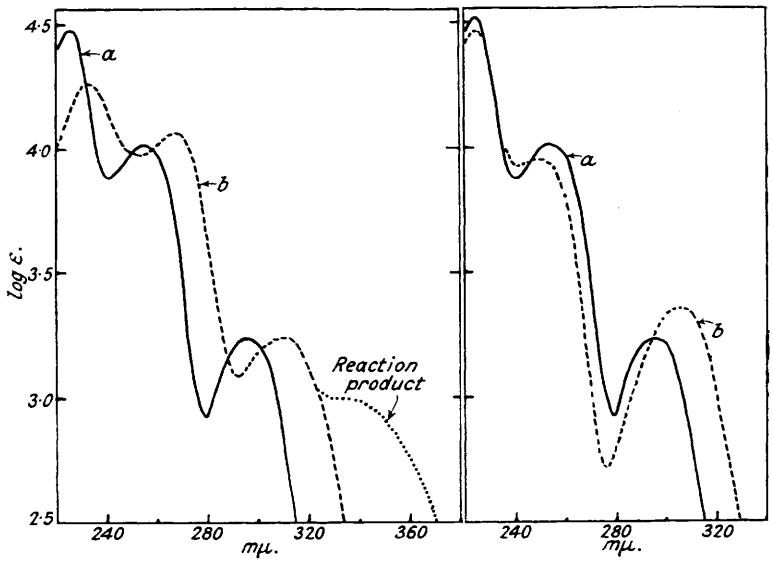
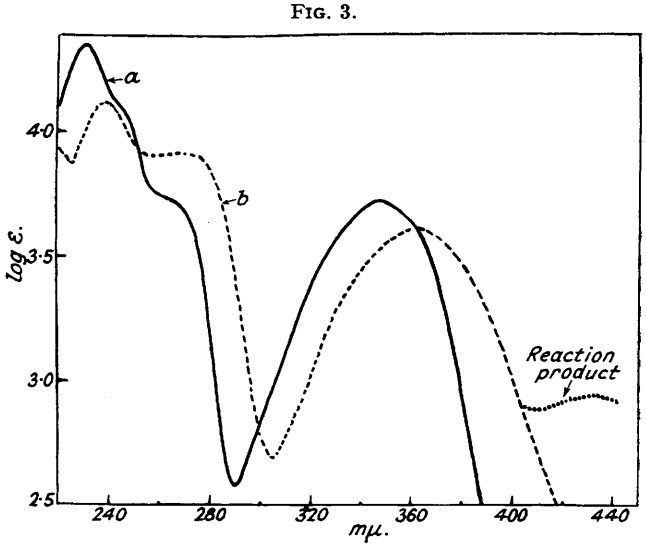


FIG. 1.—*a*, 1 : 4-*Diketo*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. *b*, 1 : 4-*Naphthaquinone dichloride*.
FIG. 2.—*a*, 1 : 4-*Diketo*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. *b*, β-*Hydrojuglone acetate*.

FIG. 3.



a, β-*Hydrojuglone*. *b*, *Juglone dichloride*.

recently that the antihæmorrhagic sodium hydrogen sulphite addition product of 2-methyl-1 : 4-naphthaquinone has structure (X) since its absorption spectrum is very similar to that of 2-methyl-1 : 4-naphthaquinone 2 : 3-oxide (XI). Both curves are very similar to that of (VI; R = Me). Macbeth, Price, and Winzor (*J.*, 1935, 325) have shown that the spectra of simple 1 : 4-naphthaquinones have a maximum at *ca.* 330 mμ.: introduction of a *peri*-hydroxyl group moves the absorption bands towards the red, but when such hydroxyl groups are acetylated the spectra revert to the simple form. β-Hydrojuglone and its acetate show the same effect (Figs. 2 and 3). The curves also show that saturation of the 2 : 3-double bond of the naphthaquinones shifts the maximum at *ca.* 330 mμ. to *ca.* 300 mμ. and introduces a new band at very short wave-length (225 mμ.). For juglone, saturation of the 2 : 3-double bond moves the peak at 425 mμ. to 347 mμ. and again a new maximum is introduced at a short wave-length (230 mμ.).

Although the ability of naphthols and certain polyhydric phenols to react in the tautomeric keto-form is well known, the existence of simple dihydroxynaphthalenes in a stable diketo-form has not hitherto been recognised, except in cases where the ketonic and enol forms are obtained by different chemical procedures and are not interconvertible. *E.g.*, 1 : 4-naphthaquinone dichloride (VIII) is the ketonic isomer of 2 : 3-dichloro-1 : 4-dihydroxynaphthalene (VII). All attempts to tautomerise these compounds failed. Enol ⟶ keto-conversion by fusion of the enol form is not possible as the diketone decomposes above its melting point, and the reverse change cannot be brought about by solution in dilute alkali as (VIII) immediately loses hydrochloric acid under these conditions. Heating solutions of the halogen compounds in the presence of catalysts and under ultra-violet radiation did not promote tautomerisation.

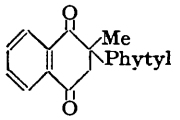
Fusion of 1 : 4-dihydroxynaphthalene, or its 2-methyl derivative, yields an equilibrium mixture containing *ca.* 10% of the diketo-form, whereas α-hydrojuglone is converted into the β-isomer in 67% yield by this method. Reduction of naphthazarin with acid stannous chloride yields a diketone directly in 90% yield. β-Hydrojuglone may also be obtained by direct reduction of juglone with acid stannous chloride, but the method fails completely with 1 : 4-naphthaquinone and its 2-methyl derivative and only the dihydroxy-compounds are obtained. The greater ease of formation of β-hydrojuglone is probably a further effect of intramolecular hydrogen bonding which would enhance the stability of the diketo-form, and this is more marked in (V) which contains two hydrogen bonds. On fusion of α- and β-naphthol in a vacuum no change was detected.

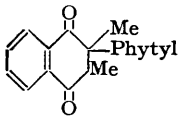
The diketones (VI; R = H and Me), and the corresponding dienols appear to exist in solution as such and there is no sign of an equilibrium. The hydrojuglones on the other hand can exist as an equilibrium mixture in aqueous solution, and α-hydrojuglone may be partly converted into the β-isomer by boiling an aqueous or an aqueous-acid solution, preferably in the presence of a reducing agent to prevent oxidation of the α-form to juglone. When Mylius (*loc. cit.*) isolated both α- and β-juglone from unripe walnut shells the first extraction was carried out with dilute hydrochloric acid containing a little stannous chloride. The aqueous solution obtained was then extracted with ether, and the residue left after removal of the solvent was boiled repeatedly with large amounts of water containing stannous chloride to extract the two hydrojuglones. Clearly isolation of β-hydrojuglone under these conditions is no evidence of its existence in Nature, and the work of Daglish (*loc. cit.*) establishes that β-hydrojuglone is not a natural product. Mylius indeed claimed to have isolated the two hydrojuglones from *ripe* walnut shells, although at one stage he oxidised the extract, isolated juglone, and subsequently reduced it with stannous chloride.

The preparation of hydroxy-diketones analogous to (IV) and (V) by condensing phenols with succinic anhydride in an aluminium chloride–sodium chloride melt is claimed in G.P. 454,762. This method is satisfactory with *p*-dihydric phenols but difficulty would be expected with phenol itself. Examination of the crude product described yielded a little β-salicyloylpropionic acid, but no β-hydrojuglone could be detected. Cyclisation of β-aroylpropionic acids to form naphthalene derivatives is not likely to occur as these compounds readily form lactones. β-Benzoylpropionic acid, for example, forms a lactone when heated alone or with dehydrating agents (Fittig and Ginsberg, *Annalen*, 1898, **299**, 17). When cyclisation of the last acid was attempted using anhydrous hydrogen fluoride the organic acid was recovered unchanged.

Although both carbonyl groups of these diketones are free to enolise, active-hydrogen determinations showed that this takes place only to a limited extent under the Zerewitinoff conditions. Thus β-hydrojuglone and (VI; R = H) did not react with the Zerewitinoff reagent in the cold, but when warmed liberated methane equivalent to 1·53 and 0·95 active

hydrogen atoms respectively; (VI; R = Me) liberated 0·33 equivalent of methane in the cold. Similar results were obtained by Tishler, Fieser, and Wendler (*J. Amer. Chem. Soc.*, 1940, **62**, 1982) with more complex compounds of the same series. By measuring the amount of Grignard reagent consumed *by addition to carbonyl groups* as well as the amount of methane liberated they obtained results corresponding to one hydroxyl group and one carbonyl group in the case of (XII), whereas (XIII) yielded a neglible amount of methane (*i.e.*, virtually no enolisation) but two equivalents of Grignard reagent were used.

(XII.) 



(XIII.)

The simple diketotetrahydronaphthalenes appear at first sight to have promising synthetic applications, but unfortunately the compounds exhibit few ketonic properties, and under most reaction conditions they enolise readily and yield only naphthol derivatives. Thus the diketones (VI; R = H or Me) failed to condense with benzaldehyde or *p*-nitrobenzaldehyde, in contrast to *cyclo*hexane-1 : 4-dione which condenses with benzaldehyde to form 2-benzylquinol (Stollé and Möring, *Ber.*, 1904, **37**, 3487), and Brockmann and Müller (*Annalen*, 1939, **540**, 51) found that the more stable diketone (V) would condense with aliphatic aldehydes, the initial product rearranging to an alkylnaphthazarin. The only products isolated from Grignard and Reformatsky reactions were the corresponding dihydroxynaphthalenes, and reduction with lithium aluminium hydride and the Ponndorf reagent had the same result. Condensation of (VI; R = H) with *p*-nitrosodimethylaniline yielded 2-(*p*-dimethylaminoanilino)-1 : 4-naphthaquinone. Investigation showed that the initial reaction was an oxidation of the enolised diketone to 1 : 4-naphthaquinone, and reduction of the nitroso-compound to *p*-aminodimethylaniline, followed by normal 1 : 4-addition. With (VI; R = Me) reaction with *p*-nitrosodimethylaniline did not proceed beyond the oxidation stage. Madinaveitia (*Anal. Fis. Quim.*, 1933, **31**, 750) has reported that 1 : 4-additions are much more difficult with 2-methyl-1 : 4-naphthaquinone than with 1 : 4-naphthaquinone, and Fries and Lohmann (*Ber.*, 1921, **54**, 2912) observed that 2-methyl-1 : 4-naphthaquinone did not react with aniline. This has been confirmed, and likewise *p*-chloro-, *p*-nitro, and *p*-dimethylamino-aniline failed to react. This is possibly a steric effect as methylamine has been added successfully to 2-methyl-1 : 4-naphthaquinone (Asano and Hase, *J. Pharm. Soc. Japan*, 1941, **61**, 55).

Experimental.

5-Hydroxy-1 : 4-diketo-1 : 2 : 3 : 4-tetrahydronaphthalene (*β-Hydrojuglone*).—This was prepared (*a*) by Willstätter and Wheeler's method (*loc. cit.*), the intermediate α-hydrojuglone being isolated more conveniently by pouring the ethereal solution through a layer of anhydrous sodium sulphate into light petroleum and collecting the crystalline precipitate rapidly (yield, 67%).

(*b*) A suspension of juglone (1 g.) in dilute hydrochloric acid (250 c.c.; 12%) containing stannous chloride (5 g.) was refluxed for 1 hour, forming a pale yellow solution which was repeatedly extracted with chloroform. After several extractions the yellow colour disappeared but reappeared on storage as the equilibrium was restored. The chloroform solution yielded 0·65 g. of β-hydrojuglone.

(*c*) α-Hydrojuglone (0·5 g.) in dilute hydrochloric acid (50 c.c.; 4%) containing stannous chloride (2·5 g.) was refluxed for 30 minutes. On cooling, the light-yellow solution deposited colourless needles of unchanged α-compound. Chloroform-extraction yielded 95 mg. of the β-isomer (Found: Active H, 0·87%).

β-Hydrojuglone crystallises from hexane in light yellow needles or plates, m. p. 96—97°, and from alcohol in pale yellow leaflets (not colourless, as described by Mylius). The *mono-p-nitrophenylhydrazone* crystallised from a large volume of acetone in small yellow needles, m. p. 270° (decomp. after blackening from 260°) (Found: C, 61·85; H, 4·2; N, 13·9. $C_{16}H_{13}O_4N_3$ requires C, 61·7; H, 4·2; N, 13·5%). A Javanovsky reaction gave a blue-green colour becoming violet. Attempts to prepare a di-*p*-nitrophenylhydrazone by refluxing the compound with excess of reagent in various solvents with and without mineral acid yielded a very insoluble dark purple-brown solid which charred without melting and could not be purified (Found: N, 15·0. $C_{22}H_{18}O_5N_6$ requires N, 18·8%). No satisfactory product could be obtained by using other carbonyl reagents.

1 : 4-Diketo-1 : 2 : 3 : 4-tetrahydronaphthalene.—This was obtained by fusion of 1 : 4-dihydroxynaphthalene in a vacuum according to Olay (*loc. cit.*). It formed colourless leaflets (from hexane), m. p. 98° (10·5%; starting material recovered, 55%) (Found: Active H, 0·63%). The *mono-p-nitrophenylhydrazone* crystallised from alcohol in short orange-red needles, m. p. 255° (decomp.), and gave a blue Javanovsky reaction (Found: C, 65·3; H, 4·5; N, 14·5. $C_{16}H_{13}O_3N_3$ requires C, 65·1; H, 4·4; N, 14·2%). The *di-p-nitrophenylhydrazone* separated from *o*-dichlorobenzene in minute rust-red needles, m. p. 284° (decomp.) (Found: C, 61·7; H, 4·4; N, 19·5. $C_{28}H_{18}O_4N_6$ requires C, 61·4; H, 4·2; N, 19·5%). It gave a violet Javanovsky reaction.

1 : 4-Diketo-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene.—This was prepared by Olay's procedure. The

diketone crystallised from hexane in small colourless leaflets, m. p. 60° (11%; 1 : 4-dihydroxy-2-methylnaphthalene recovered, 60%) (Found : Active H, 0·19%. Analysis by Drs. Weiler and Strauss). The *mono*-p-*nitrophenylhydrazone* crystallised from dilute acetic acid in rust-red small crystals, m. p. 242° (decomp.), and gave a deep-blue Javanovsky reaction (Found : C, 66·3; H, 5·0; N, 13·5. $C_{17}H_{15}O_3N_3$ requires C, 66·0; H, 4·9; N, 13·6%). The *di*-p-*nitrophenylhydrazone* formed small orange crystals (from aqueous acetone), m. p. 295° (decomp.), and gave a reddish-violet Javanovsky reaction (Found : C, 62·4; H, 4·7; N, 18·8. $C_{23}H_{20}O_4N_6$ requires C, 62·2; H, 4·5; N, 18·9%).

Reactions of the Diketones.—The above diketones failed to give characteristic colour reactions with ferric chloride, sodium nitroprusside, or 3 : 5-dinitrobenzoic acid, dissolved slowly in dilute sodium hydroxide (β-hydrojuglone dissolved rapidly), but gave no indication of unsaturation with bromine. There was no reaction with acetic anhydride during 24 hours at room temperature, or on warming the mixture for 2 hours at 95°, in the absence of a catalyst. On addition of a trace of concentrated sulphuric acid there was an immediate reaction at room temperature. β-Hydrojuglone formed a monoacetate, and the other diketones the corresponding 1 : 4-diacetoxynaphthalenes. All three diketones failed to react with diazomethane. With phenyl *iso*cyanate no reaction took place in boiling xylene (3 hours) in absence of a catalyst, but addition of a drop of triethylamine to a mixture of diketone and phenyl *iso*cyanate caused an immediate reaction at room temperature with formation of the corresponding di- and tri-phenylurethanes. Identical compounds were obtained from the dienols, using the same catalyst.

β-Hydrojuglone acetate. To a stirred suspension of β-hydrojuglone (250 mg.) in acetic anhydride (0·5 c.c.) cooled in ice, a trace of concentrated sulphuric acid was added. The yellow suspension became rapidly colourless. After 10 minutes the acetate was collected, washed with light petroleum, and dried. When crystallised from methanol (charcoal) it formed colourless needles, m. p. 144° (Found : C, 65·7; H, 4·6; Ac, 21·0. $C_{12}H_{10}O_4$ requires C, 66·0; H, 4·6; Ac, 19·7%).

When the acetic anhydride filtrate was stirred with a little ice, a white precipitate was obtained. Crystallisation from dilute acetic acid afforded colourless needles of 1 : 4 : 5-triacetoxynaphthalene, m. p. and mixed m. p. 130°.

1 : 4-*Dihydroxynaphthalenebisphenylurethane* crystallised from alcohol in colourless needles, m. p. 220° (Found : C, 72·0; H, 4·5; N, 6·9. $C_{24}H_{18}O_4N_2$ requires C, 72·35; H, 4·55; N, 7·0%).

1 : 4-*Dihydroxy-2-methylnaphthalenebisphenylurethane* formed colourless needles (from glacial acetic acid), m. p. 238° (Found : C, 72·6; H, 5·1; N, 6·6. $C_{25}H_{20}O_4N_2$ requires C, 72·8; H, 4·9; N, 6·8%).

1 : 4 : 5-*Trihydroxynaphthalenetrisphenylurethane* separated from aqueous dioxan in small colourless crystals, m. p. 298° (Found : C, 71·1; H, 4·2; N, 7·8. $C_{31}H_{23}O_6N_3$ requires C, 69·8; H, 4·35; N, 7·9%).

2-(p-*Dimethylaminoanilino*)-1 : 4-*naphthaquinone.*—A solution of (VI; R = H) (160 mg.) and *p*-nitrosodimethylaniline (150 mg.) in methanol (3 c.c.) was refluxed for 30 minutes, by which time a large mass of crystals had separated. Crystallisation from light petroleum (b. p. 100—120°) afforded small purple-brown needles, m. p. 203° (decomp.) (250 mg.) (Found : C, 74·3; H, 5·2; N, 9·6. $C_{18}H_{16}O_2N_2$ requires C, 74·0; H, 5·5; N, 9·6%). Identical material was obtained by heating 1 : 4-dihydroxynaphthalene with *p*-nitrosodimethylaniline, or 1 : 4-naphthaquinone with *p*-aminodimethylaniline, in alcohol. The *amino-quinone* formed a red solution in concentrated sulphuric acid, and gave a royal-blue colour in alcoholic sodium hydroxide. Hydrolysis with 50% sulphuric acid yielded 2-hydroxy-1 : 4-naphthaquinone, yellow needles (from aqueous alcohol), m. p. and mixed m. p. 192—194° (decomp.) (acetate, m. p. and mixed m. p. 128°).

A solution of 1 : 4-dihydroxynaphthalene (or the corresponding diketone) (0·8 g.) and *p*-nitrosodimethylaniline (0·75 g.) in alcohol (25 c.c.) was raised to the boil. When the reaction had subsided the solution was cooled and poured into dilute sulphuric acid. The precipitate which formed was collected, yielding, after steam-distillation, yellow needles, m. p. and mixed m. p. with 1 : 4-naphthaquinone, 125° (0·7 g.). Addition of dimethylaniline and aqueous potassium dichromate to the acid filtrate gave the deep-green colour of Bindschedler's green. When 2-methyl-1 : 4-dihydroxynaphthalene (or the diketone) was heated with *p*-nitrosodimethylaniline in boiling alcohol for 1 hour dark crystals separated on cooling. Recrystallisation from water yielded pale yellow needles of 2-methyl-1 : 4-naphthaquinone, m. p. 106°.

Absorption Spectra.—The ultra-violet absorption spectra were determined in alcohol. As the quinone dichlorides react with alcohol the curves were plotted in sections as rapidly as possible. The absorption was read backwards from 400 to 290 mμ., after which the region 400—450 mμ., was examined giving a new curve owing to formation of chloroquinone (dotted line in the Figs.).

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